

## THE MEASUREMENT OF WATER TIGHTLY BOUND BY LOW RANK COALS

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Schafer<sup>1</sup> has suggested that low rank coals retain water after being nominally dried at 110°C. This paper discusses the results of direct determinations of water present in "dry" coals and the possible effects of tightly bound water on the measured physical, chemical, and conversion properties of coals.

A coal characterization program at the Baytown, Texas Labs of Exxon Research and Engineering Company employed a sample library of 66 samples ranging from lignites to low volatile bituminous coals.<sup>2,3</sup> Apparent densities of the samples measured in polar organic probes (methanol, isopropanol, and methyl ethyl ketone) were much higher than densities determined in helium. These differences appeared to be related to coal rank and the polarity of the solvents. However, densities determined in water (more polar than the organic solvents) were within experimental error equal to density determinations in helium.

Franklin<sup>4,5</sup> reported that the differences between densities determined in methanol and helium were proportional to the heat of wetting of methanol on coal and to the surface area of the coal. Walker, et. al.<sup>6</sup> reported that a significant fraction of the surface area of low rank coals may be covered with carboxyl groups. Thus, apparent heat of wetting might reflect interactions of methanol and carboxyl groups. In addition, Schafer reported that dried coals decarboxylate under mild pyrolysis (175°C) to yield CO<sub>2</sub> and H<sub>2</sub>O.<sup>1</sup> It is also known that small amounts of water can be incorporated into large excesses of methanol without apparent volume change.<sup>7</sup> These observations lead us to formulate the following hypotheses: (1) water is bound tightly by low rank coals and is not removed by drying overnight in a vacuum; (2) the bound water is extracted by methanol refluxing, and (3) the bound water affects density measurements.

### Experimental

Carboxyl group contents were determined for the library samples using a modification of Schafer's ion exchange.<sup>8</sup> Samples of -325 M coal were washed with citric acid to remove metallic cations. Samples of 0.5 g were then refluxed in 0.5 N barium acetate at 50°C for 24 hrs under N<sub>2</sub>. Solutions were back-titrated with BaOH to 8.5 pH.

To study the amount of tightly held water in dried coals, a ten-sample subset of the Exxon Coal Library was chosen on the basis of carboxyl group content. Aliquots of the raw and citric acid washed coals from the subset were dried overnight in a vacuum oven at 110°C. Vacuum was broken with N<sub>2</sub> and the samples transferred immediately into a glove box. After cooling, three grams of each sample were transferred to boiling flasks, 150 ml of methanol was added to the samples, and the mixtures refluxed for one hour. Prior to mixing, the methanol had been dried over 3A type molecular sieves and blank reflux tests were conducted. All transfers and subsequent refluxing were performed under nitrogen. Following reflux, the methanol extract was decanted. The residue was dried and weighed to determine the total weight extracted during refluxing. The density of the methanol extracts were determined at 30°C by pycnometry, and the water content in the methanol extract was determined by a Fisher Aquatest.<sup>9</sup>

In every case, the weight of the solid residue after refluxing and removal of methanol was within one percent of the starting weight of coal minus correction for the extracted "bound" water assayed by the Aquatest in the methanol.

## Results and Discussion

As illustrated by Figure 1, one mole of water can be removed by  $\text{CH}_3\text{OH}$  refluxing of the "dried", raw\* coal for each molar equivalent of carboxyl groups as determined by barium exchange of acid-washed coal. For "dried", acid washed coals, approximately one-half as many water molecules are held after drying as there are carboxyl groups. Approximately 0.2 milliequivalents of water per gram of coal is retained by the coals which contain very little or no carboxyl groups.

The results indicate that water is held by low rank coals even after drying overnight in a vacuum oven. Refluxing in excess methanol removes this water. Also, when some carboxyl groups are in a salt form, more water is held than when all the groups are in an acid form. Assuming that other typical coals contain carboxyl groups with similar proportions of cations exchanged to them, the amount of water held by raw coals can be approximated by the number of carboxyl groups present in the (acid washed) coal. The carboxyl groups present in coals can be estimated by the following equation derived from the Exxon library data base:

$$\text{COOH}_{\text{dmmf}} = 19.4 - 0.222 \cdot \text{C}_{\text{dmmf}} - 0.0173 \cdot \text{VIT}_{\text{VOL}} \quad (1)$$

where  $\text{COOH}_{\text{dmmf}}$  = Carboxyl content (meq/g) (dry mineral free)  
 $\text{C}_{\text{dmmf}}$  = Carbon content of coal (%) (dry mineral free)  
 $\text{VIT}_{\text{VOL}}$  = Vitritine content (VOL. %, mineral-free)

The correlation coefficient squared ( $r^2$ ) is 0.94, and the equation predicts  $\text{COOH}$  to within  $\pm 0.1$  meq/gram (dry mineral free coal basis).

Densities of the water-containing methanol solutions were determined by pycnometry. The densities of these solutions were proportional to the amount of bound water extracted; apparently no measurable volume change occurred when the water was incorporated into a large excess of methanol. Densities of extracts from methanol reflux measured at  $30^\circ\text{C}$  ranged from 0.783 g/ml to 0.789 g/ml with a mean of 0.786 g/ml for the 20 samples tested. Densities of the methanol blanks dried over 3A molecular sieves averaged 0.783 g/ml. Reproducibility of the density measurements was better than  $\pm 0.0005$  g/ml. The measured densities of the mixture, within experimental error, results from the addition of the water to the mixture without changing the volume of the mixture.

Water bound to the oven-dried coal would be extracted into the large volume of any polar liquid during density determinations; therefore, apparent densities measured in these polar liquids would be spuriously high. Water bound in the coal would be weighed, but its volume would not be measured. When the density of coal is determined in helium, water, n-hexane, or toluene, the bound water would be weighed and its volume would be measured. However, since the density of tightly held water is lower than the densities of coals (assuming that the

\*Raw refers to state of the coal after preparation such as grinding and washing but prior to any chemical treatment such as acid washing.

density of the tightly held water is that of bulk water), the density of the solid material measured in these probes is lower than its true density. Also, since water will repel hydrophobic hexane and toluene, complete filling of the pore structure will not occur. Densities of the library coals determined in hexane and toluene are less than densities measured in helium.

Figure 2 demonstrates the effects of tightly bound water on the density of coals measured in methanol and in helium. In Figure 2, methanol densities are plotted as a function of helium densities. A parity line is included for reference. Apparent densities determined in methanol (squares) are based on the assumption that the density of the bulk methanol does not change during the density determination. The open circles represent corrected helium and methanol densities calculated from apparent densities, assuming that water is incorporated into bulk methanol without changing the volume of the bulk liquid, that the moles of tightly bound water present in the coal are equal to the moles of carboxyl groups in the coal, and that chemically held water has a density of bulk water. Correcting apparent densities for the tightly held water does not bring the corrected densities to the parity line, but differences between the corrected densities determined in the two media are much smaller.

Numerous explanations have been presented in the literature to account for differences in densities measured in various media. These are summarized as: (1) opening of pores by removal of various organic components causes methanol densities to be greater;<sup>10,11,13</sup> (2) the differences in average molecular size of the probe causes differences in apparent densities;<sup>11,12</sup> (3) Vander Waals contraction of methanol occurs on the coal surface during the density determination;<sup>4,5</sup> (4) incorporation of solvent into the gel-like structure of coals occurs, causing an increase in density due to solvent-polymer interactions.<sup>12</sup> These factors can now be more satisfactorily applied because the differences which need to be explained range from 0.01 g/ml to 0.05 g/ml on the corrected basis instead of the 0.03 g/ml to 0.15 g/ml range for apparent densities where tightly held water is not taken into account.

In addition to the effects of tightly held water on apparent densities, the tightly held water may affect other physical properties. If polar functional groups project from the pore walls, significant interactions between the functional groups and polar probes by vapor adsorption could result in increases in the coal swelling through the disruption of intermolecular hydrogen bonding. Because bound water helps spread the charge density over a longer distance, its presence could enhance these interactions. Also, because pore volume calculated from equilibrium moisture volume is greater than pore volume calculated from particle and real densities, water swells the coals. Thus, the swelling volume attributed by some workers to "plastic swelling by solvent vapors" is, in part, due to disruption of secondary bonding<sup>14,15,16</sup> that releases compression strain and creates larger pores. Second, if water is incorporated nonvolumetrically into the swelling solvent, solvent uptake on a weight percent basis will be affected because the water incorporated into the solvent leaves a void volume to be filled by the solvent. The weight gain is interpreted as a solvent-solid interaction instead of the water-solvent interaction. Third, hydrophobic solvents are repelled by the presence of water on the surface of the pores. Thus, the solvent is not incorporated into the bulk coal, which in the absence of bound water, the solvent might otherwise penetrate.

The presence of water might affect surface properties. For example, if solvent incorporates water into its bulk nonvolumetrically, a heat release would occur. Corrections for this heat release should be considered when studying the heat of wetting of solvents on coal surfaces. The presence of tightly held water may affect the contact angle between the coal and a wetting agent. Because particle densities and pore volumes are determined by mercury intrusion and calculated on the basis of contact angle, they could be in error.

Tightly held water is not measured in standard procedures that call for moisture determination by drying at 110°C for one hour. Therefore, any procedure that calls for correction of results based on determined moisture content does not adjust data properly. ASTM tests, such as the Btu content, volatile matter yields and elemental analyses are corrected for ASTM water only and are not corrected for the tightly held water which is present in the starting coal. In elemental analysis, water is weighed as part of the actual sample, then the sample is burned and the products of the combustion (water and CO<sub>2</sub>) are trapped and measured. Tightly held water as well as ASTM moisture and water of combustion are also trapped. This procedure calls for an adjustment of the hydrogen content based on the ASTM water, but no adjustment is made for tightly held water. Therefore, the hydrogen in the tightly held water is assigned as organic hydrogen in the coal. The starting weight includes oxygen from the tightly held water which is incorporated in the calculations as oxygen by difference and assigned to the organic content of the coal.

Correcting the chemical analyses for tightly held water results in a change of as much as 0.5% in hydrogen content. The hydrogen to carbon ratio changes by as much as 0.075, and the oxygen to carbon ratio changes by as much as 0.03. The net result is that the relative positions of compositions of coals on a van Krevelen diagram change. These changes in relative position affect the concepts of coal metamorphism and average molecular structures.

The presence of tightly held water may affect chemical activity of the coal in three ways. First, water will react with certain reagents that react with coal structure. For example, water will hydrolyze Grignard reagents that would otherwise attack esters and ketones in the coals forming alcohols. It will also react with trifluoroacetic anhydride to form acetic acid during titrations for OH groups in the coals. Second, water will affect diffusion properties. For example, water bound to pore walls will restrict pore apertures and thus increase diffusional resistance of certain chemical reactions. Third, by being closely associated with the carboxyl groups, the water may effectively block reactions such as esterification.

Finally, quantitative results from analytical spectroscopic methods such as Fourier Transform Infrared Spectroscopy (FTIR) are calculated on the weight of the sample in the analyzed pellets. Because tightly bound water is present in varying amounts in each coal, each sample's spectrum should be corrected for that bound water. At present, standard techniques do not. Also, because the OH stretch of the bound water would absorb in the same regions of the spectrum as do acid functionalities, the acid (OH) content of the coal is overestimated by this technique.

Material and heat balances of conversion processes should account for tightly held water. For example, some water present in liquefaction products will be formed from bound water; therefore, heats of liquefaction should be adjusted accordingly. Also, the bound water may influence total yields and yield pattern in liquefaction, pyrolysis, and hydropyrolysis. Other processes such as grinding, dispersion of catalysts, cleaning, and coking may be affected by the presence of the tightly held water.

## Conclusions

Coals dried by conventional techniques contain water that can be removed by polar organic solvents during refluxing. The incorporation of water into the solvents can lead to erroneous density determinations in polar organic solvents. The bound water is proportional to the carboxyl group content of the coal. Because lower rank coals contain more carboxyl groups than higher rank coals, the effects of bound water are more profound in lower rank coals. The presence of water on coals assumed to be dry could have far reaching significance in other areas of coal science such as solvent coal swelling, elemental analysis, coal classification, chemical activity, processing yields, and heat balances. We would recommend that such possible effects be kept in mind when treating data on presumably dry coals.

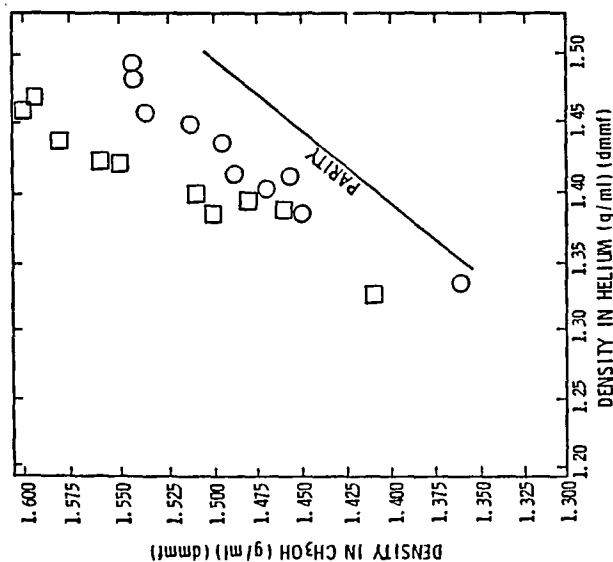
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FIGURE 2

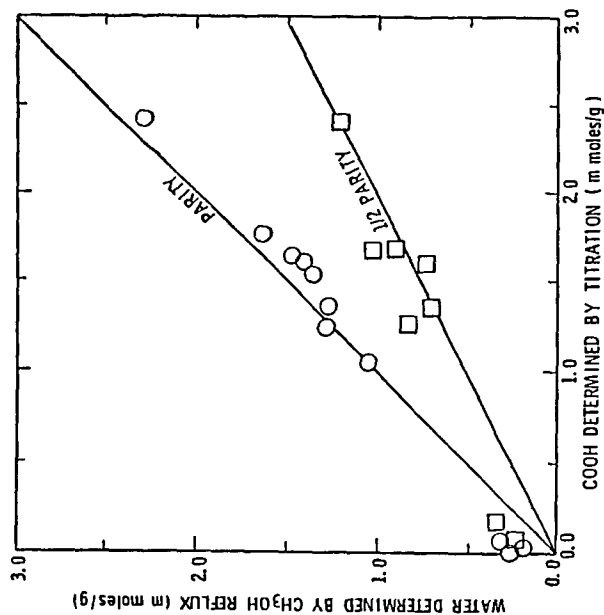
BOUND WATER EFFECT ON DENSITY



- Density Corrected for Bound Water Based on the Assumptions that:
  - Water Is Incorporated Into Bulk  $\text{CH}_3\text{OH}$  Without Volume Change
  - Chemisorbed Water has Density of Bulk Water
- Density as Determined In Methanol

FIGURE 1

RELATIONSHIP BETWEEN ABSORBED WATER AND CARBOXYL GROUPS



- Water Determined on "Dry", Raw Coals
- Water Determined on "Dry", Acid Washed Coals